

06298 PCT (WHEG P9098WO)  
09/2004

-31-

## CLAIMS

10/524325  
DT01 Rec'd PCT/PTC 11 FEB 2005

1. A process for producing higher molecular weight hydrocarbon compounds or oxygenates from a gas comprising methane, said process comprising:

5 generating synthesis gas ("syngas") comprising carbon monoxide and hydrogen by reaction of a gas comprising methane with steam and/or an oxidant gas comprising oxygen;

producing higher molecular weight hydrocarbon compounds or oxygenates  
~~in a syngas conversion process;~~

10 removing offgas comprising unreacted hydrogen and unreacted carbon monoxide from said syngas conversion process; and

separating unreacted hydrogen from said offgas or from a gas derived therefrom to produce separated hydrogen product, wherein unreacted hydrogen is separated in a cryogenic separation process to produce separated hydrogen

15 product that is substantially free of unreacted carbon monoxide and a first cryogenic liquid comprising unreacted carbon monoxide, characterised in that the process further comprises:

separating unreacted carbon monoxide from said first cryogenic liquid or from a cryogenic liquid derived therefrom in a cryogenic distillation column to  
20 produce separated carbon monoxide product and substantially carbon monoxide-free cryogenic liquid.

2. A process as claimed in Claim 1 wherein the cryogenic separation process is a liquid methane wash.

25 3. A process as claimed in Claim 1 or Claim 2 wherein higher molecular weight hydrocarbon compounds are produced, said process further comprising using separated hydrogen product for hydrogenation of a fraction of said higher molecular weight hydrocarbon compounds to produce liquid hydrocarbon  
30 compounds.

BEST AVAILABLE COPY

06298 PCT (WHBG P9096WO)  
09/2004

-32-

4. A process as claimed in Claim 3 wherein said separated hydrogen product is used in the hydrogenation of said hydrocarbon fraction without purification.

5. A process as claimed in any of Claims 1 to 4 further comprising recycling separated carbon monoxide product for conversion into higher molecular weight hydrocarbon compounds or oxygenates.

6. A process as claimed in any of Claims 1 to 5 wherein said first cryogenic liquid further comprises argon, said process further comprising removing at least one argon-enriched stream from a location in the region of high argon concentration in the cryogenic distillation column.

7. A process as claimed in any of Claims 1 to 6 wherein the substantially carbon monoxide-free cryogen liquid is substantially pure liquid methane, said process further comprising recycling a vaporised portion of said substantially pure liquid methane for conversion into syngas.

8. A process as claimed in any of Claims 1 to 7 wherein said offgas further comprises helium, said process further comprising separating helium from said separated hydrogen product using a membrane separation system.

9. A process as claimed in any of Claims 1 to 8 wherein said offgas further comprises low molecular weight hydrocarbon compounds, said process further comprising:

cooling said offgas or a gas derived therefrom to condense said low molecular weight hydrocarbon compounds to produce liquefied petroleum gas ("LPG") and removing said LPG to produce substantially LPG-free offgas; cooling and at least partially condensing said substantially LPG-free offgas to produce partially condensed substantially LPG-free offgas; and

BEST AVAILABLE COPY

06298 PCT (WHBG P9096WO)  
09/2004

-33-

separating unreacted hydrogen from a vapour portion of said partially condensed substantially LPG-free offgas in said cryogenic separation process to produce said separated hydrogen product and said first cryogenic liquid.

- 5 10. A process as claimed in Claim 9 wherein unreacted hydrogen is present in said first cryogenic liquid, said process further comprising separating unreacted hydrogen from said first cryogenic liquid or a cryogenic liquid derived therefrom in a further cryogenic separation process to produce separated hydrogen fuel by-product and a second cryogenic liquid comprising unreacted carbon monoxide.

10

11. A process as claimed in Claim 10 wherein the further cryogenic separation process is a liquid methane wash.

12. A process as claimed in Claim 10 or Claim 11 wherein said offgas further  
15 comprises helium and wherein separated hydrogen product is recycled for conversion into higher molecular weight hydrocarbon compounds, said process further comprising removing a portion of said separated hydrogen product once the concentration of the helium in the separated hydrogen product is between from 1 mol % to 20 mol %.

20

13. A process as claimed in Claim 12 wherein said portion is adjusted in flowrate so that the helium concentration reaches the required concentration.

14. A process as claimed in any of Claims 1 to 13 further comprising at least  
25 partially vaporising liquid nitrogen ("LIN") to provide refrigeration duty to keep the process in heat balance.

15. A process as claimed in any of Claims 1 to 14 wherein the oxidant gas is oxygen with a purity below 99 mol % produced in an integrated cryogenic air  
30 separation process, said LIN being produced in said air separation process.

BEST AVAILABLE COPY

06298 PCT (WHBG P9096WO)  
09/2004

-34-

16. A process as claimed in any of Claims 1 to 15 wherein separated hydrogen product is recycled for conversion into higher molecular weight hydrocarbon compounds.

5 17. A process as claimed in any of Claims 1 to 16 wherein said syngas is generated by partially oxidizing natural gas with oxygen and by reforming natural gas with steam.

~~18. A process as claimed in any of Claims 1 to 17 wherein said syngas~~  
10 conversion process is a Fischer-Tropsch ("FT") process.

19. Apparatus for the production of higher molecular weight hydrocarbon compounds or oxygenates from a gas comprising methane according to the process as defined by Claim 1, said apparatus comprising:

15 a syngas generation system for generating syngas comprising carbon monoxide and hydrogen by reaction of a gas comprising methane with steam and/or an oxidant gas comprising oxygen;

a syngas conversion system for converting syngas into higher molecular weight hydrocarbon compounds or oxygenates and producing offgas comprising  
20 unreacted hydrogen and unreacted carbon monoxide; and

a cryogen separation system for separating unreacted hydrogen from said offgas or a gas derived therefrom to produce separated hydrogen product that is substantially free of unreacted carbon monoxide and a first cryogenic liquid comprising unreacted carbon monoxide,

25 characterised in that the apparatus further comprises:

a cryogenic distillation column for separating unreacted carbon monoxide from said first cryogenic liquid or from a cryogenic liquid derived therefrom to produce separated carbon monoxide product and substantially carbon monoxide-free cryogenic liquid.

20. Apparatus as claimed in Claim 19 wherein the cryogenic separation system is a first liquid methane wash column.

21. Apparatus as claimed in Claim 19 or Claim 20 producing higher molecular weight hydrocarbon compounds, said apparatus further comprising a hydrogenation system for hydrogenating a fraction of said higher molecular weight hydrocarbon compounds using separated hydrogen product to produce liquid hydrocarbon compounds.

22. Apparatus as claimed in any of Claims 19 to 21 further comprising conduit means for feeding separated carbon monoxide product from said cryogenic distillation column to said syngas conversion system.

23. Apparatus as claimed in any of Claims 19 to 22 further comprising conduit means for removing an argon-enriched stream from a location in the region of high argon concentration in said cryogenic distillation column.

24. Apparatus as claimed in any of Claims 19 to 23 wherein said substantially carbon monoxide-free cryogenic liquid is substantially pure liquid methane, said apparatus further comprising conduit means for feeding substantially pure liquid methane from said cryogenic distillation column to said syngas generation system.

25. Apparatus as claimed in any of Claims 19 to 24 wherein the offgas further comprises helium, said apparatus further comprising a membrane separation system for removing helium from separated hydrogen product.

26. Apparatus as claimed in any of Claims 19 to 25 wherein unreacted hydrogen is present in said first cryogenic liquid, said apparatus further comprising a second liquid methane wash column in which unreacted hydrogen is separated from said first cryogenic liquid or a cryogenic liquid derived therefrom to produce

08298 PCT (WHBG P9096WO)  
09/2004

-38-

separated hydrogen fuel by-product and a second cryogenic liquid comprising unreacted carbon monoxide.

27. Apparatus as claimed in Claim 26 wherein said offgas further comprises helium and wherein separated hydrogen product is recycled for conversion into higher molecular weight hydrocarbon compounds or oxygenates, said apparatus further comprising conduit means for removing a portion of said separated hydrogen product having a concentration of helium between from 1 mol % to 20 mo %.

10

28. Apparatus as claimed in any of Claims 19 to 27 wherein the syngas generation system comprises a partial oxidation ("POX") reactor and an enhanced heat transfer reformer ("EHTR").

29. Apparatus as claimed in any one Claims 19 to 28 wherein the syngas conversion system comprises at least one FT reactor.